

(43) International Publication Date 22 February 2001 (22.02.2001)

PCT

# (10) International Publication Number WO 01/12889 A1

- (51) International Patent Classification<sup>7</sup>: B32R 5/25, D06N 7/00, A410 31/00
- D04H 13/00,
- (21) International Application Number: PCT/US(00/21922
- (22) International Filing Date: 1) August 2000 (11,08,2000)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 09/373,863

13 August 1999 (13.08.1999) US

- (71) Applicant: GORE ENTERPRISE HOLDINGS, INC. [US/US]; 551 Paper Mill Road, P.O. Box 9206, Newark.
- (72) Inventors: GUNZEL, Edward; 3602 Christian Meadows, Bear, DE 19701 (US). JAIN, Mukesh; 297 Shisler Court, Newark, DE 19702 (US).

- (74) Agents: CAMPBELL, John, S. et al., W. L. Gore & Associates, 551 Paper Mill Road, P.O. Box 9206, Newark, DE 19714-9206 (US).
- (81) Designated States (national): AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, PI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LE, LU, LY, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, BO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW.
- (84) Designated States fregionali: European pinem (AF, BE, CH, CY, DE, DK, ES, FI, FR, GB, GB, IE, IT, LU, MC, NL, PT, SE).

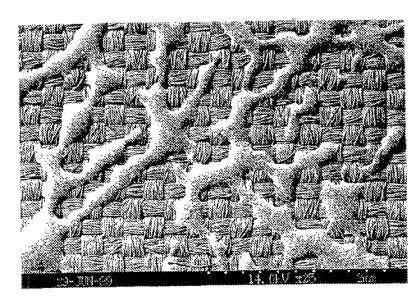
#### Published:

With international search report.

Por two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginuing of each regular issue of the PCT Greette.

(54) Title: TREATED FABRIC

DE 19714-9206 (US).



(57) Abstract: This invention is directed to fabrics with good abrasion resistance. The fabric used in the invention is a woven or knot fabric made from yarn, either single or multiple strand. A very light application of polymen, e.g., between about 5 and 40 g/m<sup>3</sup>, is applied to the fabric surface to improve abrasion resistance, usually by applying a non-woven light weight web of a melt blown, spunbonded polymeric material, or by melt blowing or spraying a polymeric material directly onto the fabric to form a web. The fabric with the polymer now on the surface can then be optionally heated so that the filaments of the web melt and lose their fibrous nature.



## TITLE

## TREATED FABRIC

5

#### FIELD OF THE INVENTION

This invention relates to fabrics and garments of improved abrasion resistance.

10

13

20

25

30

35

#### BACKGROUND

Garments for outerwear are typically subject to harsh conditions in use. As a result of this exposure, shell fabrics are often designed to provide a variety of properties including waterproofness, windproofness, water and stain repellency, moisture vapor permeability (breathability), as well as aesthetic qualities such as soft hand and fashionable appearance. Activities such as backpacking, rock climbing, kayaking, hunting, fishing, and even everyday use, expose the garments, particularly the shell, to a variety of environments that tend to abrade and wear the fabric. Thus, the desirable protective and aesthetic qualities will be compromised in use.

Typically fabric type (e.g., polyester, nylon, polypropylene, etc.) and weight are selected based on the end use (e.g., backpacking, fishing, general use, etc.). For example, nylon fabrics are typically used in backpacking and rock climbing applications because of their better durability. In particular, the heavier weight nylons (2 oz/yd2 or greater) are used because of the abrasion resistance required in these demanding activities. However, it is known in the art that nylon typically has inferior water repellency compared to polyester. Yet, polyester cannot be used in many activities that require durable water repellency, because of its poor abrasion resistance. Thus the current art of textiles in outerwear tends to restrict the selection of textiles, sometimes producing less than optimal results for backpacking, where durable water repellancy is important, polyester cannot be used.

In order to protect from abrasion, continuous coatings are typically employed using polymers such as silicones, polyurethanes, polyvinylchloride, and the like. However, these coatings tend to alter the appearance and hand of the fabric. They also tend to impede or prevent breathability. As is known in

ŝ

10

13

20

25

30

the art, high breathability is important to the wearer's comfort and, in extreme situations, to a wearer's survival. Conventional methods of applying a continuous coating to a fabric fill the interstices between yarns, rendering the fabric stiff and often compromising the breathability. In addition, such a coating changes the appearance from a textile look to a film look.

In order to maintain breathability, discontinuous coatings have also been used. Patterns such as honeycombs, grids, and discrete dots have been put into practice to a limited extent on the inside of shell fabrics. (See Blauer et al., U.S. Patent 5626949.) However, a significant limitation of using such coatings on the outside of a garment is the change in appearance caused by the macroscopic and regular pattern of the coating, which is undesirable because the textile appearance is undesirably aftered. A further limitation of using regular patterns is that disruptions in such patterns are prone to scrutiny. Any deviations in the regularity associated with processing, or that develop in use can have undesirable aesthetic effect. Finally, the periodicity associated with regular patterns can introduce stress concentrations along preferred axes, which can tend to cause accelerated wear in those areas.

#### SUMMARY OF THE INVENTION

The present invention overcomes the problems described above by providing a polymer treated fabric with significantly improved abrasion resistance over the untreated fabric with very minimal weight add-on. In addition, the minimal weight add-on and discontinuous nature of the polymer on the fabric maintains substantially the breathability (water vapor transmission) and the aesthetic appearance of the underlying fabric. The present invention also provides garments using such fabrics and process for obtaining them.

The fabric used in the invention is a woven or knit fabric made from yam, either single or multiple strand.

A very light application of polymer, e.g., between about 5 and 40 g/m<sup>2</sup>, preferably 5 and 30 g/m<sup>2</sup>, is applied to the fabric surface, usually by applying a non-woven light weight web or by melt blowing or spraying a polymeric material directly onto the fabric to form a web.

10

3

20

25

30

35

The web on the fabric is caused to melt so that the filaments of the web lose their identity. Depending on the temperature at application, this may occur spontaneously so that application of heat is not needed. On the other hand, the fabric with the polymer now on the surface can be subsequently heated so that the filaments of the web melt and lose their fibrous nature.

Several surface configurations of the polymer can be obtained, depending on the degree and time of heating. For example, at shorter heating periods, the non-woven web melts into irregularly shaped protective patches of polymer randomly interconnected or unconnected. At longer heating times, the web melts into a thin coating that is thin enough that the pattern of the fabric surface is still visible, and forms a thin layer on the uppermost portion of yarn and does not substantially occlude a majority of the spaces between the yarns.

Whatever the polymer configuration on the surface of the fabric, the fabric maintains good moisture vapor transmission, being greater than 1000 g/m².24 hours. Moreover, the hand of the original fabric is substantially maintained. The abrasion resistance of the treated fabric is very good, as opposed to the abrasion resistance of the original fabric, which ordinarily has a much lower abrasion resistance.

The treated fabric of this invention can be used in any application where resistance to abrasion of a fabric is desirable, particularly where breathability, flexibility, and aesthetic properties are important. Such applications include but are not limited to garments, tenting, backpacks, footwear, bivy bags, and other protective coverings or shelters, and the like.

More specifically, the invention can be described in one aspect as a fabric construction comprising

- a). a woven or knit fabric comprised of yam,
- b) said fabric having adhered to its surface a discontinuous, randomly disposed polymeric material;
   such that the resulting composition has
  - i). a moisture vapor transmission rate of at least 1000 g/m²/day.
  - ii) a abrasion resistance of at least 100 cycles determined on the polymer side, and
  - an add-on weight of between 5 and 40 g/m<sup>2</sup>.

20

30

in another aspect, the construction comprises adhering the polymeric material to a laminate of the fabric and an underlying porous, water-resistant, water vapor permeable film or membrane. In this aspect, apparently due to the lamination effect, the abrasion resistance will be at least 300 cycles, preferably 500 cycles or more.

## BRIEF DESCRIPTION OF THE DRAWINGS

- Fig. 1 is an SEM of the MI 260 polyamide treated fabric of Example 2 in taken at 25X.
  - Fig. 2 is an SEM of the same fabric taken at 100X.
  - Fig. 3 is an SEM of the MI 260 fabric laminate used in Example 4 after melt blown polyurethane was blown on, but before heat treatment.
  - Fig. 4 is an SEM of the melt blown MI 260 fabric laminate of Example 4, but after heat treatment at 140°C, taken at 25X.
  - Fig. 5 is an SEM of the melt blown MI 260 fabric laminate of Example 4, but after heat treatment at 200°C taken at 25X.
  - Fig. 6 is an SEM of the melt blown MI 260 fabric laminate of Example 4, after heat treatment at 200°C taken at 100X.
  - Fig. 7 is an SEM cross section of the melt blown Mi 260 fabric laminate of Example 4 after heat treatment at 200°C taken at 200X.

## **DEFINITIONS**

- By fabric is meant a material made from textile fibers or yarns,
- 25 By yarn is meant twisted threads of natural or synthetic fibers used to weave or knit a fabric.
  - By water resistant is meant that the material in question passes the water resistance test described further below.
  - By water vapor permeable is meant that the material in question has a water vapor permeability of at least 1000 g/m²/day.
  - By abrasion resistance is meant that the material in question lasts at least 300 cycles in the test described below.
  - By garment is meant any article that can be worn, including footwear, hats, gloves, shirts, coats, trousers, etc.
- 35 By shell is meant an outer layer of fabric.
  - By discontinuous is meant that there are areas of substrate surface that are not covered by polymer.
  - By random is meant unpatterned.

WO 01/12889 PCT/US00/21922

## DETAILED DESCRIPTION OF INVENTION:

This invention provides a fabric that possesses significantly improved abrasion resistance with minimal weight add on, so that breathability and hand are not significantly impeded. The polymeric material on the surface of the fabric is deposited in a manner that does not adversely affect the aesthetic qualities. Surprisingly, by applying only 5 to 40 g/m² polymer add-on, the abrasion is often improved by 50-100% or higher, e.g., 1000% or more, with little to no effect on breathability.

30

20

25

30

The advantage of using the polymeric construction defined here to create an abrasion resistant fabric is based both on economics and performance. To improve abrasion resistance of fabrics typically requires an increase in the weight of the fabric. From a performance perspective, the increased weight is undesirable and often imparts increased bulk and stiffness which in turn compromises packability. From the standpoint of economics, polyester fabrics tend to be less expensive than nylon fabrics, but the major drawback to using polyesters in performance outerwear is their poor abrasion resistance. By improving abrasion resistance, this invention can be used to produce low cost fabrics that perform like more expensive ones.

Useful as the fabric in this invention are woven or knitted fabrics that are made of yarn, either natural or synthetic, such as wool, cotton, polyamide, polyester, polyolefin, aramid and the like. The woven or knitted fabrics could have surfaces that are sanded, embossed, knapped, flocked, fleeced, etc. The fabrics used in the invention are water vapor permeable, having a moisture vapor transmission rate of at least 1000 g/m².24 hours.

The polymeric material applied to the fabric can be a polyurethane, polyamide, polyester, polyolefin, silicone, acrylic or the like. The polymer could be water-vapor-permeable, as well. This, however, is generally not necessary, provided that the percentage coverage of the fabric surface is not too great to substantially affect the water-vapor-permeability thereof.

3.5

Selection of the appropriate polymer for a given abrasion resistance will be dictated by the end use requirements and the production methods available, in general, polyurethanes are known to be excellent in resisting abrasion which make them ideal materials for applications requiring a high level of abrasion

S

10

15

20

25

30

35

resistance from the polymer layer. In addition, they can be formulated to yield a high degree of softness, making them excellent candidates where the handle of the finished composite is of concern. However, instances may arise where it becomes beneficial to use an entirely different class of polymers. In these cases, the structure of the abrasion resistant layer of this invention will still work to provide a relative level of abrasion resistance. Fillers and additives may also be used to enhance other properties or to further increase the abrasion resistance, and may be used in conjunction with any of the aforementioned processes to provide a suitable, or in some instances superior, product. Finally, polymer selection will also be affected by the type of fabric the abrasion resistant layer is being applied to. It is usually best to select a polymer to provide chemical compatibility between the polymer and the fabric, allowing for a sufficient bond. In cases where chemical compatibility is not possible, it may be beneficial to tailor the rheology and surface characteristics of the polymer to allow for sufficient wetting and/or pore penetration in order to provide sufficient mechanical bonding between the polymer and the textile surface. Instances may also arise where the substrate will allow for both mechanical and chemical bonding.

The general process employed to make the products of this invention is to apply a plurality of polymeric fibers to the surface of the fabric. Techniques such as heat treating non-woven webs into the fabric surface, as well as melt blowing and fiberizing polymer fibers directly onto the surface, can be used. Upon subsequent heat treatment, the polymeric fibers melt, losing their identity. The resulting polymeric appearance can be random, interconnected, discrete or the like, depending on the aforementioned heat treatment. A benefit of using fine, lightweight non-woven webs is the ability to create structures which minimize the distance between polymer areas, providing for better local abrasion resistance as is needed around cuffs, collars, pocket edges, and generally any folds or creases.

When the polymer is applied to the fabric by applying a preformed nonwoven web of the polymer, the web can simply be laid over the fabric and heated to a temperature which melts the polymer but not the fabric. Melting of the polymeric filaments destroys the non-woven web structure and causes formation of the discontinuous, randomly disposed polymeric material and adherence to the fabric surface.

PCT/US00/21922 WO 01/12889 7

When the polymer is applied through melt blowing or spunbonding, due to the nature of meltblowing or spunbonding, the pordus web ferming polymer is usually laid down on the substrate in the form of filaments, as shown in Fig. 3. A subsequent heating step is carried out at a temperature above the softening point of the polymer to cause the filament polymer to flow and spread to form the structures shown in Fig. 4, 5 and Fig. 6. The heating is most conveniently carried out in an oven, e.g., hot air or IR. However, if the viscosity of the polymer is low enough, or if the substrate is pre-heated, the desired structure may form on the fabric without any further application of heat.

10

15

20

25

30

33.

Another process which can be used to create the current invention is by spray fiberizing of low viscosity resins consisting of polymers, prepolymers, or oligomers (for example, using an apparatus such as the ITW Dynated's Uniform Fiber Depositor-Hendersonville, TN). This technique is similar to melt blowing, except the viscosities of the resins are generally lower and the resins typically require some post processing to build viscosity. For example, spray fiberizing a urethane pre-polymer would require a curing step (for example, heat treatment if it has a blocked isocyanate group) to build molecular weight and hence viscosity and ultimately coating integrity. Similarly, silicones would require a post heat treatment step, along with a catalyst such as platinum, to initiate polymerization and improve coating integrity, prior to taking up in a roll form.

Another process that could be employed involves the deposition of meltable discontinuous fibers or powders onto the surface of the fabric followed by subsequent melting of the particulate.

One type of product is obtained when a non-woven web is placed on the fabric and heated. This type is shown in Fig. 1 and 2 and, as seen, the result is formation of irregularly shaped patches of randomly interconnected polymer.

Another type of product is obtained when a non-woven web is formed by melt blowing or fiberized spraying, and heated. This type is shown in Figs. 4, 5, 6, and 7. The melt blown web before heating is shown in Fig. 3 where it is seen that the web is composed primarily of fibers. But when the treated fabric is heated to obtain products of the invention, it is seen that the result is a thin layer of polymeric material that becomes more uniform as the heating temperature is raised, and appears to be concentrated on the uppermost

exposed surface of the fabric yarns. It is also seen that the layer does not completely cover the fabric and in that sense is random, leaving spaces between the yarns unoccluded. Furthermore, as seen in Fig. 7, the polymeric material is concentrated primarily on the yarn surface and only somewhat penetrates into the yarn bundles.

Generally the percentage coverage of the surface of the fabric by the polymer is in the region 10-90%, more particularly 30-70. It will be appreciated that the spacing between areas of polymer should not be so great as to permit ready access to open areas whereby abrasion of these open areas may occur.

Meltblowing is one preferred method to form a polymeric, porcus web on the fabric. To form melt blown webs, a fiber forming polymer is extruded from an extruder that can have one orifice or multiple orifices directly into convergent high velocity heated air streams to produce fine filaments. The melt blown filaments are deposited on the moving substrate in an entangled, random fashion and are then fused to form a coherent coalesced porcus web of filaments. The degree of coalescing and the degree of adherence to the substrate can be furthered by subsequent heating above the softening point. It is also seen in Figs. 4, 5, and 6 that an intermediate temperature of heating displays an intermediate degree of fiber coalescing and adherence to the substrate. Heating times may be as little as a few seconds, e.g., 3 to 5 seconds, or can be longer, e.g., 30 to 60 seconds or more.

The web forming polymer is preferably chosen to be compatible with the fabric surface so that the web filaments readily adhere to the substrate surface as they are laid down or as later heated.

A thermoplastic elastomeric polyurethane polymer is one of a number of polymers that are found satisfactory for the formation of filaments in accordance with he present invention. It will be appreciated, however, that other polymeric materials can also be used provided their abrasion resistance is satisfactory for their purpose and they are able to be bonded to the fabric with which they are to be used.

35

10

15

20

25

30

The fabric, on the side opposite that on which the polymeric material is adhered, can be laminated to or coated with other layers to form a multi-layered composite. For example, the other side of the fabric may be attached or

WO 01/12889 PCT/US00/21922

Ü

adhered to a water-resistant, water vapor permeable film or membrane, such as a monolithic breathable polyurethane or polyester polyether film or a porous, especially microporous, polyethylene or polypropylene, or polyurethane. A preferred membrane or film is composed of an expanded polytetrafluoroethylene (ePTFE) membrane as disclosed in US Patent No. 3,953,566, which has a porous microstructure characterized by nodes interconnected by fibrils. The membrane is resistant to passage of liquid water therethrough but is watervapor-permeable. The membrane preferably has a weight between 1 and 100 grams per square meter.

10.

15

20

25

30

5

In a membrane or film containing ePTFE, the ePTFE can be impregnated with a hydrophobic impregnant (such as a perfluoro compound or, for example, perfluoroalkyl acrylate or methacrylate polymer.) The ePTFE may have on it a continuous layer of a film or coating of a water-resistant, water vapor parmeable material such as a water-vapor-permeable polyurethane of the type disclosed in US Patent No. 4,194,041. The continuous water vapor permeable polymer layer is a hydrophilic polymer in the sense that it transports water molecules and will be referred to herein as a hydrophilic polymer. The hydrophilic layer selectively transports water by diffusion, but does not support pressure driven liquid or airflow. Therefore, moisture, i.e., water vapor, is transported but the continuous layer of the polymer precludes the passage of liquid water and such things as air-borne particles, micro organisms, oils, or other contaminants. This characteristic imparts to the fabric good contamination control. Furthermore the water vapor transmitting characteristics of the material allow for comfort characteristics to the wearer.

Such hydrophilic polymeric materials can be those of the polyurethane family or the copolyether ester family, or like materials. Typically these materials comprise a composition having a high concentration of oxyethylene units to impart hydrophilicity, typically greater than 45% by weight of the base polymer, preferably greater than 60%, most preferably greater than 70%. The most preferred polyurethanes useful herein are those where the polyol is a poly(oxyethylene) glycol, and the isocyanate is a diisocyanate.

35 The fabric construction described hereinabove can be used in garments to improve the garment's abrasion resistance. While the construction is most useful as the outermost layer or shell of the garment, it can be used to protect

against abrasion anywhere in the garment, whether as an intermediate layer or

WO 01/12889 PCT/US00/21922

30

the innermost layer. In other words, wherever an abrasion-causing surface exists, the treated fabric of the invention can be used with the orientation of the treated side facing the abradant.

5

#### **TEST PROCEDURE**

#### **ABRASION RESISTANCE:**

Samples were evaluated for abrasion resistance, as determined by visual inspection, using a modified universal wear test method. The method is based on ASTM standard D3886-92 and consists essentially of abrading a sample with a selected abradant and determining the number of cycles until a hole visually appears through the test sample.

15

20

25

30

35

10

The sample is abraded using a Commercial Inflated Diaphragm Abrasion Tester available through Custom Scientific Instruments in Cedar Knolls, New Jersey (model no. CS59-391). A one pound weight is used along with a 4 psig inflation pressure to accelerate the wear. 600 grit sandpaper is used as the abradant. The abradant is replaced every 150 cycles and at the start of a new sample.

Circular samples, 4.25 inches in diameter, are placed on the tester with the polymer treated side of the fabric to be abraded facing up and a contrasting color substrate can be placed below to facilitate observation. The sandpaper is moved horizontally across the surface of the sample in a back and forth motion while the sample itself is being rotated 360 degrees to ensure uniform wear in all directions. A single back and forth motion is denoted as a "cycle".

The sample is evaluated for visual wear every 50 cycles until a hole through the sample is observed. The point of the first sign of a hole is recorded as abrasion failure, in the case of the two layer and three layer water proof, breathable laminate used to create the examples 2 through 6, the white, microporous ePTFE membrane provided adequate contrast to indicate the failure point (when the a hole through the fabric to the ePTFE was apparent). For the raw fabrics tested, an ePTFE based membrane was placed behind the fabric (adjacent to the diaphragm) to provide contrast on failure.

10

3 5

20

25

30

35

in this invention, the treated fabric will have an abrasion resistance of at least 400 cycles, but if laminated or coated, at least 300 cycles, preferably at least 500 cycles, and in some instances at least 1000 cycles.

At least two specimens were tested and the abrasion resistance is reported as the average number of abrasion cycles required for the specimens to fail.

# MOISTURE VAPOR TRANSMISSION RATE (MVTR) (Potassium Acetate Method)

Moisture vapor transmission rate (MVTR), i.e. water-vapor-permeability, was measured by placing approximately 70 ml of a solution consisting of 35 parts by weight of potassium acetate and 15 parts by weight of distilled water into a 133 ml. polypropylene cup, having an inside diameter of 6.5 cm at its mouth. An expanded polytetrafluoroethylene (PTFE) membrane having a minimum MVTR of approximately 85,000g/m2/24 hrs. as tested by the method described in US Patent No. 4,862,730 to Crosby and available from W. L. Gore & Associates, Inc. of Newark, Delaware, was heat sealed to the lip of the cup to create a taut, leakproof, microporous barrier containing the solution.

A similar expanded PTFE membrane was mounted to the surface of a water bath. The water bath assembly was controlled at 23°C plus or minus 0.2°C, utilizing a temperature controlled room and a water circulating bath. The sample to be tested was allowed to condition at a temperature of 23°C and a relative humidity of 50% prior to performing the test procedure. Three samples were placed so that each sample to be tested was in contact with the expanded PTFE membrane mounted over the surface of the water bath, and was allowed to equilibrate for at least 15 minutes prior to the introduction of the cup assembly.

The cup assembly was weighed to the nearest 1/1000g and was inverted onto the center of the text sample.

Water transport was provided by the driving force between the water in the water bath and the saturated salt solution providing water flux by diffusion in that direction. The sample was tested for 15 minutes and the cup assembly was then removed, and weighed again to within 0.001g.

WO 01/12889 PCT/US00/21922

12

The MVTR of the sample was calculated from the weight gain of the cup assembly and was expressed in grams of water per square meter of sample surface area per 24 hours.

3

#### TEST FOR HAND:

Hand was tested on woven fabrics using a Thwing-Albert Handle-O-Meter (model # 211-5 from Thwing Albert Instrument Company, Philadelphia, PA). A 1000 gram beam was used to force test specimens through a 1/4 inch slot. The instrument measures the resistance force which is related to the bending stiffness of the fabric and displays the peak resistance digitally. In order to adequately quantify the directionality and the asymmetry of the laminate composites, different samples are cut for bending against the warp yarns and fill yarns, respectively.

15

25

30

35

30

In a typical test, a warp sample is placed on the equipment such that the warp yarns run perpendicular to the slot. With the fabric face up, the test is initiated, causing the beam to lower and the sample to be forced through the slot on the test table. A peak resistance number is displayed and recorded as warp up. The same sample is subsequently turned over (in the case of a two layer laminate, the membrane is face up) and rotated 180 degrees to bend a different site. In this new configuration, again the test is initiated causing the sample to be forced through the slot. The second resistance number is recorded as warp down. The procedure is repeated for a fill sample (in which the fill yarns are perpendicular to the slot), generating two more numbers: fill up and fill down. The resultant four numbers (warp and fill up, warp and fill down) are added to provide a total hand number which characterizes the stiffness of the fabric, laminate, or composite (taking into account asymmetry and directionality). At least two such total hand numbers were generated and averaged to arrive at the hand numbers displayed in the Examples.

#### WATER-RESISTANCE TEST

Samples of the materials were tested for waterproofness by using a modified Suter test method, which is a low water entry pressure challenge. The test consists essentially of forcing water against one side of a test piece and observing the other side of the test piece for indications of water penetration through it.

PCT/US00/21922 WO 01/12889 13

#### EXAMPLES:

The polyester woven fabrics used to create the following examples were sourced from Milliken Corporation (Spartanburg, SC). The nylon woven fabrics were sourced from Duro Industries (Fall River, MA).

## Example 1:

10

15

20

25

35

5

Two raw nylon fabrics were used to create this example: Mi160 (1.6 oz/yd2) and MI 230R (2.3 oz/yd2).

A 20°x14" sample of the Mi160 was pinned onto a pin frame and a 17"x14" piece of a polyamide non-woven adhesive web (PA-1001-090-060, 1 oz./yd. (30g/m2) from Spunfab® Adhesive Fabrics, Cuyahoga Falls, OH) was laid over the fabric. The pin frame was inserted into a convection oven (Mathis Lab Dryer-model # LTE 24296) pre-set to 180 degrees Celsius. The MI160/polyamide non-woven combination were heat treated at 180 C for 30 seconds dwell time (which is time at temperature).

A similar procedure was used to create a composite based on the MI230R fabric. The resulting composites maintained some of the fabric qualities, though it was noticeably more stiff. The non-woven web was bonded well to the fabric in each case, as it could not be easily removed by scraping. In addition, the non-woven structure was not apparent as the heat treatment destroyed the non-woven creating a fabric with a randomly coated appearance. Universal abrasion and MVTR measurements (using procedures described above) were made on these samples as well as the untreated controls (results in table #1). Weight increases due to polymeric add-on were measured using at least two 4.25 inch diameter samples and comparing to the control. Any increase in weight over the control is reported as an increase in face fabric weight (or knit weight where specified). Results are reported in Table 1.

## Preparation of Fabric Laminates Used in Subsequent Examples

Expanded polytetrafluoroethylene, hereafter referred to as ePTFE, manufactured according to U.S. Patents 3,953,566, and 4,187,390 of 15-17.

10

15

25

36

35

gm/m2 weight was coated with a continuous 12-15g/m2 layer of VVVP hydrophilic polyurethane as described in U.S. Patent 4.194,041. The resulting membrane will hereinafter be referred to as a coated ePTFE membrane.

To create a two layer laminate a polyester US101 (2.2 oz/yd2) face fabric was laminated to the ePTFE side of the coated ePTFE membrane using a dot pattern of polyurethane adhesive as described in U.S.Patent 4,532,316.

The resultant laminate is a water vapor permeable, waterproof laminate.

Similarly, two layer laminates were created by laminating a coated microporous ePTFE membrane to the following nylon fabrics: MI260 (2.4 oz/yd2), MI141R (1.4 oz/yd2), MI321 (3.2 oz/yd2), MI187R (2.0 oz/yd2) and MI160 (1.6 oz/yd2).

To create a three layer laminate, a knit was laminated to the hydrophilic polyurethane coated side of the coated ePTFE membrane on the two layer MI160 and MI187R laminates.

## 20 Example 2:

In a similar manner to that described in Example 1, a 1 oz/yd² polyamide non woven web PA-1001-090-60 (from Spunfab®) was heat treated into the face fabric of a two-layer MI260 laminate (nylon face fabric, 2.4 oz/yd²) and a two layer US101 laminate (polyester face fabric, 2.2 oz/yd²), independently.

The treatment was carried out at a temperature of 170 degrees Celsius for 30 seconds (dwell time). The resultant composites showed intimate bonding between the face fabrics and the non-woven web, to the point where the structure of the non-woven web was hardly distinguishable.

In addition, the Spunfab web was heat treated into the knit side of a three layer MI187R laminate to provide improved abrasion to the knit. The samples as well as the untreated controls were tested for weight, MVTR, and universal abrasion (results in table #2). Figures 1 and 2 show the treated fabric.

S

10

15

## Example 3:

Following a similar procedure to examples 1 and 2, a 0.5 oz/yd² copolyester-polyether non-woven web (Demique® from Kimberly Clark Corporation Roswell, GA) was laid onto a two layer Mi260 laminate (nylon face fabric) on a lab scale pin frame. The two layers were heat treated in the oven at 220 degrees Celsius for 30 seconds (dwell time). The resultant composite revealed partial infiltration of the non-woven into the Mi260. The composite maintained the flexibility (hand) of the laminate while providing a random appearance. The MVTRs, weights, and universal abrasion numbers for both the treated sample and the untreated control were measured and are recorded in table #2.

From the data in tables 1 and 2, there is seen a clear improvement in abrasion resistance independent of fabric type and weight. The advantage is applicable to both raw fabric and laminates, as well as to both knits and wovens. In particular, this example shows that it is possible to significantly improve abrasion resistance without adding significant weight or adversely affecting breathability or hand.

30

25

30

#### Example 4:

A thermoplastic polyurethane, TPU1, was synthesized from 4,4'-diphenylmethane disocyanate (MDI) / polycaprolactone diol / 1,4-butane diol in the molar equivalents of 2:1:1.12 respectively using conventional polyurethane synthesis technique and then converted into pellets. The resulting polyurethane had a melt flow index of about 140 gm/10 min. (at 195°C, 5kg).

A meltblowing die, 60 inches wide, with 0.014 inches diameter orifices arranged in a single row with a spacing of 30 holes per inch was used. The polyurethane, in pellet form, was fed into a 3 inch single screw extruder along with 2.5% of a color concentrate (Clariant Remafin Black CEA 8020A). The extruder temperature profile was maintained at 460°F and the extruder fed the melt into a gear pump set at 24 rpm to provide a steady flow of the melt to the die orifices at a throughput of 168 lbs./hr. The die nose piece was setback by 0.060 inches and the air gap was set at 0.060 inches. The air temperature was maintained at 520°F. Air velocity is based on volume of 980 cubic feet per

PCT/US00/21922

minute and the die temperature was set to 470°F. A water spray was used to quench the melt blown polyurethane,

The above conditions were used to melt blow TPU1 filaments onto the fabric side of the two layer MI141R and MI250 laminates which moved over a collector at about 84 meters/min. The collector was located 5.5 inches from the die. Under these conditions, about 12 gm/m2 of TPU1 filaments was deposited on the laminate.

Four samples of the melt blown treated fabric pre-composite were heat treated (two heat treatment conditions for each of two laminates); MI 141R and MI260 heat treated at 140 degrees Celsius for 30 seconds and MI141R and Mi250 heat treated at 200 degrees Celsius for 30 seconds (Mathis lab oven). The resultant composite possessed a surface that appeared to be a randomly coated textile, as shown in Figs. 4, 5, 5, and 7. The fibrous non-woven structure of the melt blown textile (see Fig. 3), was not apparent. The samples produced were tested for MVTR, weights, universal abrasion and hand. Results are given in table #3.

## Example 5:

3

10

15

20

25

30

A free standing 10 g/m2 melt blown polyurethane web was made using similar conditions to example #5. Blue color concentrate from Clariant was added to the melt at a concentration of 2.5% by weight. In producing the melt blown web a spunbonded polypropylene web was used as a collector substrate. This melt blown polyurethane web was subsequently heat treated into fabrics as follows.

A two layer Mi321 was placed on the Mathis pin frame and heat treated in a manner similar to examples 1 through 3 (except the non-woven web used was the PU described above). The 10 g/m2 melt blown PU web was laid on the face of the MI 321 and subsequently heat treated into the surface of the substrate at 180 degrees Celsius for 60 seconds (dwell time). The test results are given in Table 4.

PCT/US00/21922

#### Example 6:

10

35

20

25

A reactive prepolymer was prepared from diphenylmethane diisocyanate, polytetramethylene glycol and pentanediol as per the teachings of US 4,532,316 to Henn, incorporated herein by reference. The prepolymer was sprayed onto MI260 laminate produced in example 2 using a spray gun. These polymers continue to react with moisture over time and build molecular weight.

in preparation for spraying, the polyurethane was heated to 100 C in an air circulated oven in a sealed can. Part of it was then scooped out and filled into the canister of the adhesive spray gun (PAM500-K-Spray made by Pam Fastening Technology Inc. Charlotte, NC 28266 USA, Division of Buehnen Group, West Germany). The dispenser part of the gun had a single hole with an annular air ring. The air pressure was 90 psig and temperature was set to 250°F.

Spraying was performed on the fabric side of the laminate by holding the gun about 10 inches above the sample and moving back and forth using smooth motion to get a uniform lay down of adhesive web. Three passes were made to get sufficient thickness of polymer coating. Following coating, the samples were allowed to moisture cure for 48 hours before testing. These samples were tested for MVTR, universal abrasion and weight. The results are given in table 4.

In the subsequent tables the Ex#refers to the example number and the number following the hyphen is an arbitrary number assignment for samples within a given example number.

Table 1

	Table 1: Polyamide Web Treated Abrasion Resistant Composites (Raw Fabrics)	on Resistant Con	nposites (Raw Fabr	icai
		Face Fabric	Universal Abrasion	MVTR (g/m².24
Sample	Description	Weight (g/m²)	(cycles)	ã
EX1-1	Raw Mi 160 Control		160	38,020
EX 1.2	Raw Mil 150 Treated with PA-1001 180C			***************************************
	for 30 seconds	88	3600	28,950
EX1.3	Raw Mi 230R Control	20	130	33,860
Ex 1-4	Raw MI 230R Treated with PA-1001		***************************************	
	180C for 30 seconds	108	2480	27.430

Table 2

	Table 2: Polyamide Web Treated Abrasion Resistant Composites (I aminates)	Abrasion Resistant Co	omposites (Laminate	, Se
		Face Fabric Weight	Universal Abrasion	MVTR
Sample	Description	(3/111,2)	{cvc(es)	lasen 2.24 bed
Ex2-1	Two Layer Mt 260 Control	83	580	13,900
	Two Layer MI 260 Treated w/PA-1001		3280	13,780
Ex2.2	170C for 30 second	9		
Ex2-3	Two Layer US 101 Control	73	380	14.480
Ex2-4	Two Layer US 101 Treated w/PA-1001	107	3700	16.190
Ex2-5	Three Layer Mi 187R Control (knit side)	44 (kmit)	480	12.930
Ex2-6	Three Layer Mi 187R (knit side) Treated	77 (kmit)	2120	11,270
	w/PA-1001 170C for 30 seconds			
EX3-1	Two Layer MI 260 Control	\$	580	13.900
Ex3-2	Two Layer MI 260 Treated w/ Demique	105	086	13.770
	2200 for 30 seconds			

Hand (grams) 108 2 ئى ئ 157 88 (g/m².24 hr) Polyurethane Treated Abrasion Resistant Composites (Laminates) 12,890 11,680 11,560 13,840 13,900 13,670 MIVTR Universal Abrasion {cycles} 1920 630 880 740 989 1690 Weight (g/m²) Face Fabric \* 53 8 8 8 8 2L MI 141R Treated w/TPU1 Heat 2L MI 141R Treated w/TPU1 Heat 21. MI 260 Treated w/TPU1 Heat 21. Mt 260 Treated w/TPU1 Heat Two Layer (21.) Mil 141R Control Treated 140C for 30 seconds Treated 140C for 30 seconds Treated 200C for 30 seconds Treated 200C for 30 seconds Description 2L. Mil 260 Control Table 3: Sample Ex4-2 Ex4-3 EX4-4 EX4-5 Ex4-6 Ex4-1

Table 3

Table 4

	Table 4: Polymethane Web Treated Abrasion Resistant Composites (Laminates)	brasion Resistant	Composites (Lami	aminates
		Face Fabric Weight	Face Fabric Weight Universal Abrasion	MAYTR
Sarriple	Description	(, w/b)	(cycles)	talm ".34 her
EX5-1	EX5-1 2L MI 321 Centrol	108	800	13.790
Ex5-2	2L MI 321 Treated w/TPU1 Free Web	117	1350	13,260
	Heat treated 180C for 60 seconds	:		
EX4-4	2L MI 260 Control	20	580	13 900
EX6-1	MI 250 Treated w/Reactive PU (TF	63	2150	12,680
	moisture cured for two days)		•	

35

#### CLAIMS

- A fabric construction comprising:
  - a). a woven or knit fabric comprised of yarn,
- b). said fabric having adhered to its surface a discontinuous,
   randomly disposed polymeric material;

such that the resulting composition has

- a moisture vapor transmission rate of at least 1000 g/m²/day.
- an abrasion resistance of at least 100 cycles determined on the polymer side, and
- iii) an add-on weight of between 5 and 40 g/m<sup>2</sup>.
- 15 2. The fabric construction of claim 1 wherein the discontinuous, randomly disposed polymeric material is comprised of irregularly shaped patches of randomly interconnected polymer.
- 3. The fabric construction of claim 1, wherein the discontinuous, randomly disposed polymeric material forms a thin layer on the uppermost portion of the fabric yarns, and does not substantially occlude a majority of the spaces between the yarns.
- 4. The fabric construction of claim 1, 2, or 3 wherein the abrasion resistance is at least 500 cycles.
  - The fabric construction of claim 1, 2, or 3 wherein the add-on weight is between 5 and 30 g/m².
- 30 6. The fabric construction of claim 1, 2, or 3 wherein the polymeric material is selected from polyamide or polyester.
  - The fabric construction of claim 1, 2 or 3 wherein the polymeric material is polyurethane.
  - The fabric construction of claim 1, 2 or 3 wherein the fabric is comprised of polyester or polyamide yarn.

WO 91/12889 PCT/US99/21922

9. The fabric construction of claim 1, 2 or 3 wherein the woven or knit fabric has adhered to its other surface a water resistant, water vapor permeable film or membrane, and wherein the abrasion resistance is at least 300 cycles determined on the polymeric material side.

9

15

20

25

- 10. A garment that contains as the outermost surface, a woven or knit fabric comprised of yarn, said fabric having adhered on its outer surface a discontinuous, randomly disposed polymeric material;
- 10 such that the resulting composition has
  - a moisture vapor transmission rate of at least 1000 g/m²/day.
  - an abrasion resistance of at least 100 cycles determined on the polymer side, and
  - iii). an add-on weight of between 5 and 40 g/m<sup>2</sup>;
     said fabric disposed with the polymeric material on the outside.
  - 11. The garment of claim 10 wherein the discontinuous, randomly disposed polymeric material is comprised of irregularly shaped patches of a randomly interconnected polymer.
  - 12. The garment of claim 10 wherein the discontinuous, randomly disposed polymeric material forms a thin layer on the uppermost portion of the fabric yarns, and does not substantially occlude a majority of the spaces between the yarns.
  - 13. The garment of claim 10, 11 or 12 wherein the abrasion resistance is at least 500 cycles.
- 30 14. The garment of claim 10, 11, or 12 wherein the add-on weight is between 5 and 30 g/m<sup>2</sup>.
  - The fabric construction of claim 10, 11 or 12 wherein the polymeric material is selected from polyamide or polyester.

35

- The garment of claim 10, 11 or 12 wherein the polymeric material is a polyurethane.
- 17. The garment of claim 10, 11 or 12 wherein the fabric is comprised of

Š.

1.5

polyester or polyamide.

- 18. The fabric construction of claim 7, wherein said polyurethane comprises diphenylmethane diisocyanate, polycaprolactone dici and butane dici.
- 19. A fabric construction comprising:
  - a). a woven or knit fabric comprised of yarn having pores,
- b). said fabric having adhered to its surface and at least partially
   penetrated into the pores a discontinuous, randomly disposed polymeric material;

such that the resulting composition has

- a moisture vapor transmission rate of at least 1000 g/m²/day.
- an abrasion resistance of at least 100 cycles determined on the polymer side, and
- iv) an add-on weight of between 5 and 40 g/m².
- 20. The fabric construction of claim 19 wherein the discontinuous, randomly disposed polymeric material is comprised of irregularly shaped patches of randomly interconnected polymer.
- 21. The fabric construction of claim 19, wherein the discontinuous, randomly disposed polymeric material forms a thin layer on the uppermost portion of the fabric yarns, and does not substantially occlude a majority of the spaces between the yarns.
- The fabric construction of claim 19, 2,0 or 21 wherein the abrasion resistance is at least 500 cycles.
  - 23. The fabric construction of claim 19, 20, or 21 wherein the add-on weight is between 5 and 30 g/m<sup>2</sup>.
- 35 24. The fabric construction of claim 19, 20, or 21 wherein the polymeric material is selected from polyamide or polyester.
  - 25. The fabric construction of claim 19, 20 or 21 wherein the polymeric material is polyurethane.

- 26. The fabric construction of claim 19, 20 or 21 wherein the fabric is comprised of polyester or polyamide yarn.
- 5 27. The fabric construction of claim 19, 20 or 21 wherein the woven or knit fabric has adhered to its other surface a water resistant, water vapor permeable film or membrane, and wherein the abrasion resistance is at least 300 cycles determined on the polymeric material side.
- 10 28. The fabric construction of claim 19, wherein said polyurethane comprises diphenylmethane diisocyanate, polycaprolactone diol and butane diol.
- 29. A process for improving the abrasion resistance of the outer surface of a garment that is made of a knit or woven fabric comprised of yarn,

which comprises

20.

25

- a). treating said fabric with a polymeric material in a fashion to result in a discontinuous, randomly disposed covering on the fabric such that said treated fabric has
  - a moisture vapor transmission rate of at least 1000 g/m²/day,
  - an abrasion resistance of at least 100 cycles determined on the polymer side; and
  - iii). an add-on weight of between 5 and 40 g/m<sup>2</sup>.
- employing said treated fabric as the outer shell of a garment with the polymeric material on the outside.
- 30. A process for improving the abrasion resistance of a fabric which comprises
  - a). employing a woven or knit fabric
  - treating said fabric with a polymeric material in a fashion to result in a discontinuous, randomly disposed covering on the fabric such that said treated fabric has

WO 01/12889 PCT/US00/21922

- a moisture vapor transmission rate of at least 1000 g/m²/day.
- ii). an abrasion resistance of at least 100 cycles determined on the polymer side, and
- iii) an add-on weight of between 5 and 40 g/m².

5

10

15

20

31. Process of claim 29 or 30 wherein said treating is carried out by adhering a non-woven web to the surface of said fabric and heating to form the discontinuous, randomly disposed covering.

32. Process of claim 29 or 30 wherein said treating is carried out by spraying a liquid or molten reactive polymer onto the surface of said fabric and subsequently causing the polymer to react to form the discontinuous, randomly disposed covering.

33. Process of claim 29 or 30 wherein said treating is carried out by fibenzing or spraying the molten form of the polymeric material onto said fabric and providing heat to form the discontinuous, randomly disposed covering.

34. Process of claim 29 or 30 wherein said treating is carried out by melt blowing the polymeric material onto said fabric and providing heat to form the discontinuous, randomly disposed covering.

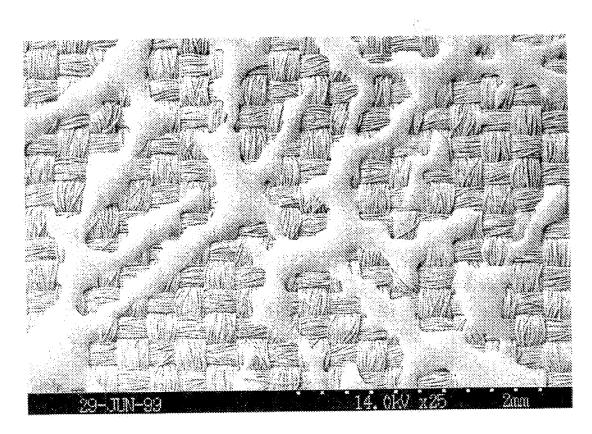


Fig 1

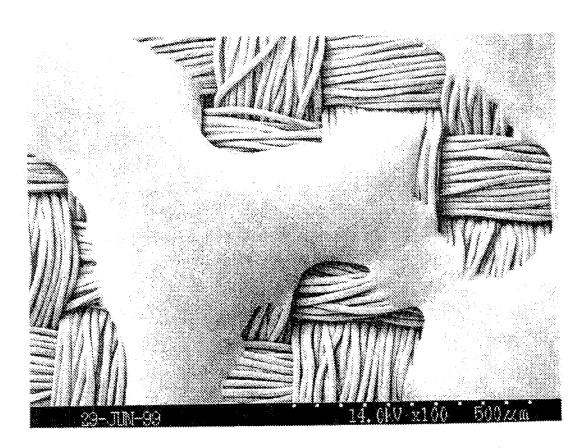


Fig 2

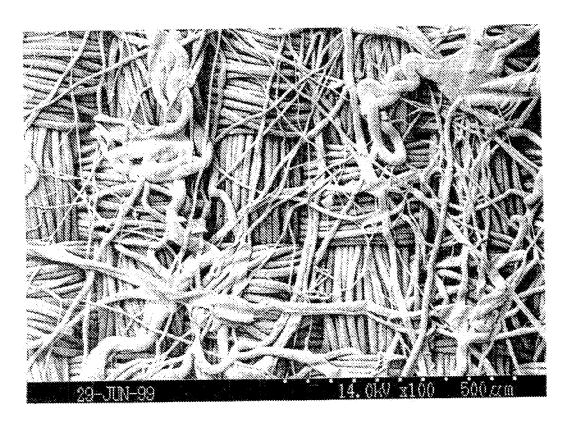


Fig 3

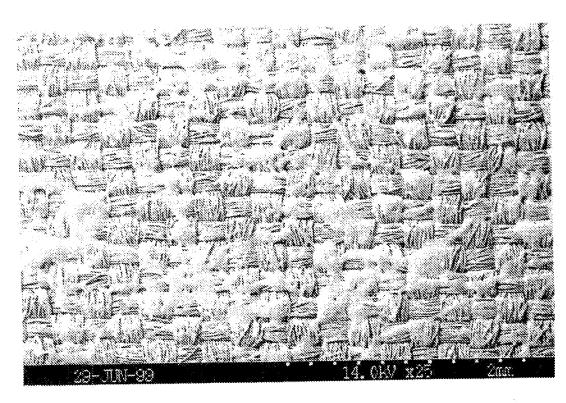


Fig 4

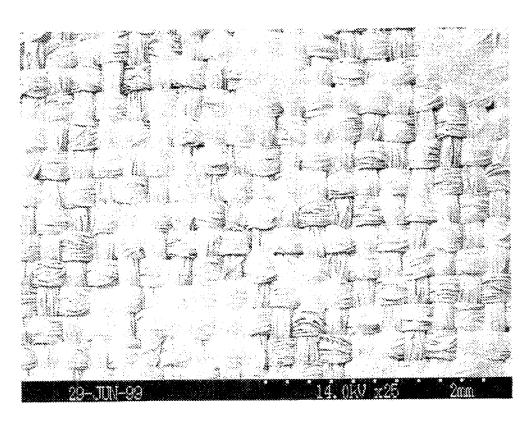


Fig 5

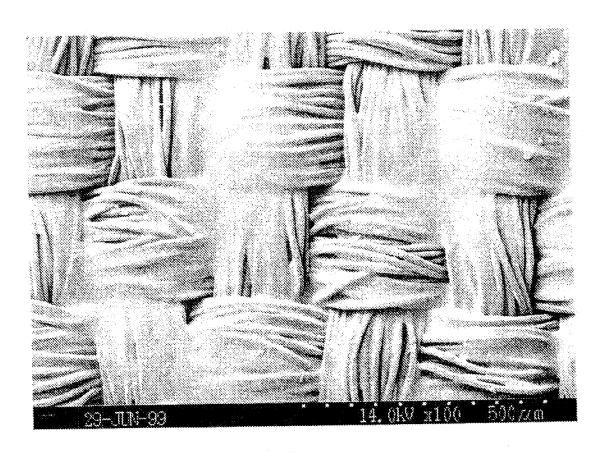


Fig 6

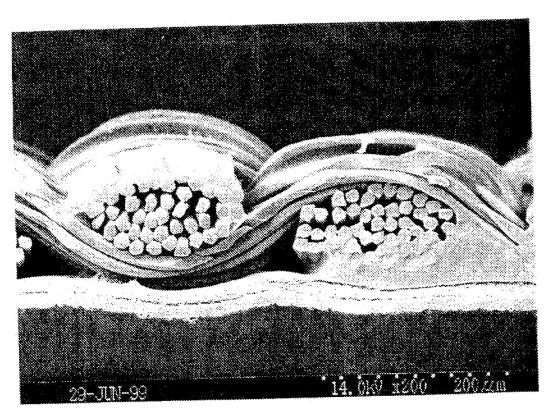


Fig7

#### INTERNATIONAL SEARCH REPORT

Intern sal Application No PCT/US 00/21922

A CLASSIFICATION OF SUBJECT MATTER IPC 7 DO4H13/00 B325 83285/26 D06N7/00 A41031/00 According to international Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by diassification symbols) DO4H 8328 006N Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data basis consulted during the international search (name of data base and where practical, search terms used) WPI Data, EPO-Internal C. DOCUMENTS CONSIDERED TO SE RELEVANT Helevant to claim No. Citation of document, with induction, where appropriate, of the relevant passages 1,3,4,7, DE 296 17 779 U (WIRZ PETER) X 8,10,12, 12 December 1996 (1996-12-12) 13,16, 17,19, 21,22, 25,26, 29-31 page 13, last paragraph; claims; figures US 5 284 677 A (COUGHLIN THOMAS E) 1,3,4, X 8-10,12, 8 February 1994 (1994-02-08) 13,17, 19,21, 22,26, 29,30,32 the whole document -/--Further documents are tisted in the continuation of box C. Patent family members are listed in entrex Special categories of ofed documents : \*T\* later document published after the international files sole or priority date and no in coeffict with the application but cled to understand the principle or theory, underlying the invention. "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier cocuming but published on or after the international "X" document of particular relevance, the claimed invention cannot be considered nevel or cannot be considered to involve as inventive step when the discurrent is taken above. Shop state \*1. document which may throw docume on priority Changs) or which is caled to establish the publication data of another "Y" document of particular relevance; the claimed invention citation or other special mason (as specified) cannel be considered to involve as investive step when the \*C\* decument referring to an onei discrease, use, exhibition or ments, such combination being obvious to a person skiller! in the art \*p\* document published point to the international filing date but later than the priority date claimed. 1&º document member of the same patent family Date of mailing of the international search report Date of the actual completion of the international search 06/12/2000 23 November 2000 Authorized officer Name and making address of the ISA European Petest Office, P.B. 5518 Patentiaan 2 NC -- 2250 HV Hijswijk Tet (+31-70) 340-2040, Tx. 31 651 epo ni Pamies Olle, S Fax: (+31-70) 340-3016

2

# INTERNATIONAL SEARCH REPORT

Intern val Application No PCT/US 00/21922

Classon of document, with indication, where appropriate, of the relevant passages  US 4 291 078 A (LYONS HAROLD D)  22 September 1981 (1981-09-22)  abstract; claims  column 2, line 4 - line 56	Florewood to cleam No.
 US 4 291 078 Å (LYONS HAROLD D) 22 September 1981 (1981-09-22) abstract: claims	1-34
column 2. line 4 - line 56 column 3, line 15 - line 34 column 3, line 67 -column 4. line 8	

## INTERNATIONAL SEARCH REPORT

...ormation on patent family members

intern sal Application No PCT/US 00/21922

Patent document cred in search repor	ŧ	Fublication date		Patent family member(s)	Publication date
DE 29617779	Ų	12-12-1996	DE	29602475 U	18-04-1996
			DE	19642251 A	14-08-1997
			DE	19642252 A	14-08-1997
			DE	19642253 A	14-08-1997
			WO	9730244 A	21-08-1997
			EP	0880628 A	02-12-1998
US 5284677	A	08-02-1994	CA	2109404 A	28-04-1994
			US	5298316 A	29-03-1994
US 4291078	A	22-09-1981	38	818677 A	10-02-1975
			CA	1033994 A	04-07-1978
			DE	2439428 A	20-03-1975
			FR	2240979 A	14-03-1975
			IT	1018890 8	20-10-1977
			JP	50048102 A	30-04-1975
			NL	7411024 A	18-02-1975
			SE	7410365 A	17-02-1975
			US	4276101 A	30-06-1981